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(21) International Application Number: PCT/US96/13637 (22) International Filing Date: 26 August 1996 (26.08.96) (30) Priority Data: 528,449 14 September 1995 (14.09.95) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, P.O. Box 710, Linden, NJ 07036 (US). (72) Inventors: DOWLING, Michael; "Sheviocke" Townsend Road, Sreatley, Berkshire RG8 9LH (GB). NOLES, Joe, Randall, Jr.; 375 Harlingen Road, Belle Mead, NJ 08502 (US). (74) Agent: BAKUN, Estelle, C.; Exxon Chemical Company, 1900 East Linden Avenue, P.O. Box 710, Linden, NJ 07036 (US).		(81) Designated States: AU, CA, JP, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: CRANKCASE LUBRICATING COMPOSITIONS (57) Abstract <p>Lubricants with improved acid neutralization properties and excellent sludge and wear performance in the Seq. 5E test are formed using a detergent system comprising one or more alkali or alkaline earth metal salts of an oil soluble organic acid selected from the group consisting of sulfonic acids, phenols, sulfurized phenols, and carboxylic acids (including salicylic acids) wherein at least one metal salt is overbased and the ratio of inorganic to organic salt present in the detergent system expressed as TBN from inorganic salts (the overbasing) to the total moles of organic salt is at least 2500. Further improvement in acid neutralization is possible by keeping the amount of dispersant nitrogen added to the basestock (independent of any nitrogen present in the basestock) below 0.053 wt.% and using a zinc dihydrocarbyl dithiophosphate system wherein at least half of the hydrocarbyl groups are secondary alkyl groups.</p>		

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Crankcase Lubricating Compositions

Field of the Invention

The present invention relates to lubricating compositions for gasoline spark ignited engine crankcases. More particularly it relates to lubricants that have particularly good acid neutralization, sludge, wear, and varnish properties and low treat rates.

Background of the Invention

Lubricants comprise basestock and additives to improve the performance of the lubricant and increase its useful life. Degradation of lubricants is known to be caused by many mechanisms including thermal and chemically catalyzed oxidation. One notorious mechanism is acid catalyzed oxidation. The acids can be sulfur containing acids formed as a byproduct of sulfur containing fuel combustion, NO_x acids formed directly from fuel combustion in the presence of air, and oxy-acids formed from degradation products of the basestock and lubricant additives. When the lubricant breaks down, free radicals are formed. Those free radicals and the aldehydes and ketones that they form can polymerize creating large viscous sludge like particles. Those particles and other products of basestock oxidation form deposits that can cause wear and make moving parts seize, for example piston rings can stick.

Antioxidants can help prevent oxidation or terminate free radicals. Dispersants can help hold sludge in solution. And antiwear compounds can prevent degradation products, including sludge, from causing wear on engine parts. Ash forming detergents neutralize acids as they are formed thereby preventing deposits and runaway oxidation.

The recent history of modern crankcase lubrication reflects ever increasing severity of demands for lubricants to control the adverse effects that result from breakdown of basestock and additives. Thus the most recent American Petroleum Institute certification level, API SH, requires lubricants to pass a panel of tests. Among the many tests required to meet the API SH classification (and its predecessor the API SG classification) are the Sequence IID (ASTM STP 315h part 1), Sequence IIIE (ASTM D553), and Sequence VE (ASTM D5302).

The Sequence IID tests an oil's ability to inhibit rust. It is intended to simulate cold winter conditions for short trip driving when condensation on the valve cover creates a corrosive environment. Acid neutralization is a key mechanism to prevent rust.

- 5 The Seq. VE (ASTM D5302) measures the lubricant's ability to prevent deposits and wear encountered during low-temperature, light duty operating conditions. Primary rating factors include measurement of sludge, varnish, and camshaft wear in the engine.

- 10 Over the years, as lubricants have continuously improved performance, the total amount of additive present in the lubricant has steadily increased. Thus typical treat rates for API SE, SF, SG and SH oils were 5.5, 6.5, 10, and 13 weight percent additive respectively.

- 15 One reason for the ever increasing amount of additive present in modern lubricants has been the phenomena of adverse interaction whereby increasing the amount of one additive adversely impacts another additive. This problem has been particularly troublesome in the area of acid neutralization. In the period beginning in April, 1994, and ending September, 1994, over 133 Sequence IID tests (ASTM STP 315h part 1) were registered with the Chemical Manufacturers Association test
20 monitoring service with a pass rate of just 52.63%.

- 25 Detergents that are used to neutralize acids generally comprise a polar head with a long hydrophobic tail, with the polar head comprising a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a
30 total base number or TBN (as may be measured by ASTM D2896) of from 0 to 80. It is possible to include large amounts of a metal base by reacting an excess of a metal compound such as an oxide or hydroxide with an acidic gas such as carbon dioxide. The resulting overbased detergent comprises micelles having neutralized organic salts as an outer layer surrounding a core of an inorganic metal base (e.g. carbonate). Such overbased detergents may have a TBN of 150 or greater, and typically of from 250 to 450 or more. The inorganic base core of the colloid is the most efficient acid neutralizer present in the lubricant.

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In practice the colloid core can only neutralize acid if the acid can be transported to it. The acid neutralization potency of a detergent system is therefore a function both of the basicity of the system and of its accessibility to acids that are formed in the lubricant. Lubricant additive manufacturers have long known that the theoretical neutralizing potency of a detergent system based on the stoichiometric amount of base present is never in fact reached. In consequence lubricants contain base in excess of that theoretically required to neutralize acid through the course of a normal drain interval, e.g. 3,000 to 6,000 miles.

Accordingly, a need exists for lubricants that have detergent systems whereby acid transport to the colloid core is improved and sustained over a normal drain interval and the overall amount of additives can be reduced without compromising performance in tests designed to monitor a lubricant's ability to handle basestock and additive degradation products.

Summary of the Invention

Lubricants with improved acid neutralization properties are formed using a detergent system comprising one or more alkali or alkaline earth metal salts of an oil soluble organic acid selected from the group consisting of sulfonic acids, phenols, sulfurized phenols, and carboxylic acids (including salicylic acids) wherein at least one metal salt is overbased and the total amount of metal salts of organic acids is minimized relative to the amount of inorganic salt in the colloid.

Further improvement in acid neutralization is possible by keeping the amount of dispersant nitrogen added to the basestock (independent of any nitrogen present in the basestock) below 0.053 wt % (grams per 100 grams of finished lubricant). Keeping the added dispersant nitrogen level between 0.0073 and 0.053 wt % and using a zinc or molybdenum dihydrocarbyl dithiophosphate system wherein at least half of the hydrocarbyl groups are secondary alkyl groups improves acid neutralization while permitting the lubricant to handle sludge well enough to pass the Seq. VE test.

A convenient way to express the ratio of inorganic to organic salt present in the detergent system is to consider the base contribution (TBN expressed as mg KOH/gm equivalents) from the overbasing relative to the

moles (or equivalents) of organic salt. Thus the ratio of TBN from inorganic salts to the moles of organic salts should be at least 2500 mg eq KOH/mole. When the amount of organic salt is minimized in this way, the amount of nitrogen is kept within the prescribed levels, and the zinc dialkyl dithiophosphate has at least 50 % secondary alkyl groups, a lubricant having a total TBN of less than 5 is possible. Obviating the need for high TBN lubricants enables a large reduction in the amount of additive required to meet the difficult performance standards of API SH certification.

Conveniently the detergent system comprises an overbased salt of an oil soluble magnesium sulfonate and the ratio of TBN from inorganic salts to TBN from organic salts is at least 4,200. Preferably the ratio of TBN from inorganic salts to TBN from organic salts is at least 7,000.

While the source of added dispersant nitrogen may be any of the conventional dispersants, typical dispersants are made by reacting a substituted succinic acylating agent with an amine wherein the substituent has a number average molecular weight (\overline{M}_n) of at least 1300. Alternatively, the source of nitrogen may be a nitrogen containing multifunctional viscosity modifier. Nitrogen may be added to the system in other ways, for example oil soluble aliphatic, oxyalkyl, or arylalkyl amines are often used to boost fuel economy and aromatic amines are often used as antioxidants. The nitrogen added in these amines should be excluded when considering the total amount of dispersant nitrogen added.

Conveniently at least 10 percent of the hydrocarbyl groups present on the metal dialkyldithiophosphate is primary. Keeping the amount of secondary hydrocarbyl groups to between 50 and 70 mole percent gives good wear performance thereby enabling reduction of the amount of dispersant nitrogen and detergent without so adversely impacting performance in fuel economy tests that the lubricant can not meet modern specifications. Most conveniently the hydrocarbyl groups are balanced in this a fashion and the total amount of phosphorus is kept below 0.1 wt percent as measured by ASTM D4927 and as defined in the proposed API PS-05 and ILSAC GF-2 specifications.

In practice, the various elements of the formulation may be added to the basestock singly or in combinations or subcombinations. Thus for example, the individual detergents that collectively comprise the detergent

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system may be added together or separately. The detergent system is present when the TBN contributions of the individual inorganic salts are summed and the moles of individual organic salts present in the individual components are summed to yield total the amounts and ratios required by the invention.

Decreasing the amount of dispersant nitrogen adversely affects the ability of an oil to hold sludge in suspension. The Seq. 5E test requires a lubricant to have good sludge dispersancy characteristics. Applicants have discovered that improving the ability of the lubricant to neutralize acids and improving the ability of a lubricant to prevent wear compensates for the adverse impact of decreasing the amount of dispersant nitrogen. This three way relationship between acid neutralization, wear, and dispersancy has not been known before. In these systems that have less detergent than typical in the past and have minimized dispersant treat rates, applicants have discovered that at least 50 % of the hydrocarbyl groups present in the zinc dihydrocarbyl dithiophosphate ("ZDDP") need to be secondary.

The low treat rate lubricant of the present invention shows surprisingly robust performance. With the present invention, a single lubricant formulation can pass all the API SH tests including the Seq. IID and the Seq. VE in a variety of basestocks with only minor formulation modifications.

Detailed Description

A. Basestock

The basestock used in the lubricating oil may be selected from any of the synthetic or natural oils used as crankcase lubricating oils for spark-ignited and compression-ignited engines. The lubricating oil base stock conveniently has a kinematic viscosity of about 2.5 to about 12 mm²/s and preferably about 2.5 to about 9 mm²/s at 100°C. The viscosity characteristic of a basestock is typically expressed by the neutral number of the oil (e.g., S150N) with a higher neutral number being associated with a higher viscosity at a given temperature. This number is defined as the viscosity of the basestock at 40 °C measured in Saybolt Universal

Seconds. The average basestock neutral number (ave. BSNN) of a blend of straight cuts may be determined according to the following formula:

$$\log(\text{ave. BSNN}) = \left[BSR_1 \times \log \frac{BSNN_1}{100} \right] + \left[BSR_2 \times \log \frac{BSNN_2}{100} \right] + \dots + \left[BSR_n \times \log \frac{BSNN_n}{100} \right]$$

where

- 5 BSR_n = basestock ratio for basestock n
 = (wt. % basestock n / wt. % total basestock in oil) x 100%
 $BSNN_n$ = basestock neutral number for basestock n

- Basestocks with lower solvent neutral numbers are used for lower viscosity grades. For example typically an SAE 5W-30 will have an ave. BSNN of 90 - 100, an SAE 10W-30 will have an ave. BSNN of 140 to 150, an SAE 10W-40 will have an ave. BSNN of 130, and an SAE 15W-50 will have an ave. BSNN of 160 - 180. Mixtures of synthetic and natural base oils may be used if desired.

B. THE METAL CONTAINING DETERGENT SYSTEM

- 15 Metal-containing or ash-forming detergents function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail, where the polar head is a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as may be measured by ASTM D2896) of from 0 to 80. It is possible to include large amounts of a metal base by reacting an excess of a metal compound such as an oxide or hydroxide with an acidic gas such as carbon dioxide. The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically of from 250 to 450 or more.

- 30 Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, salicylates, and carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in

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detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Particularly convenient metal detergents are neutral and overbased magnesium and calcium sulfonates having TBN of from 20 to 450 TBN, neutral and overbased calcium phenates and sulfurized phenates
5 having TBN of from 50 to 450, and neutral and overbased calcium and magnesium salicylates having a TBN of 50 to 450.

Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of
10 aromatic hydrocarbons. Examples include those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The
15 alkaryl sulfonates usually contain from about 9 to about 80 or more carbon atoms, preferably from about 16 to about 60 carbon atoms per alkyl substituted aromatic moiety.

The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate,
20 sulfides, hydrosulfides, nitrates, borates and ethers of the alkali metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from about 100 to 220 wt % (preferably at least 125 wt %) of that stoichiometrically required.

Metal salts of alkyl phenols and sulfurized alkyl phenols are
25 prepared by reaction with an appropriate metal compound such as an oxide, hydroxide or alkoxide and overbased products may be obtained by methods well known in the art. Sulfurized alkyl phenols may be prepared by reacting an alkyl phenol with sulfur or a sulfur containing compound such as hydrogen sulfide, sulfur monohalide or sulfur dihalide, to form
30 products which are generally mixtures of compounds in which 2 or more phenols are bridged by sulfur containing bridges. The starting alkyl phenol may contain one or more alkyl substituents. These may be branched or unbranched, and depending on the number of substituents may have from 1 to 30 carbon atoms (provided the resulting alkyl phenol is oil soluble),

with from 9 to 18 carbon atoms being preferred. Mixtures of alkyl phenols with different alkyl substituents may be used.

Metal salts of carboxylic acids (including salicylic acids) may be prepared in a number of ways: for example, by adding a basic metal
5 compound to a reaction mixture comprising the carboxylic acid (which may be part of a mixture with another organic acid such as a sulfonic acid) or its metal salt and promoter, and removing free water from the reaction mixture to form an metal salt, then adding more basic metal compound to the
10 reaction mixture and removing free water from the reaction mixture. The carboxylate is then overbased by introducing the acidic material such as carbon dioxide to the reaction mixture while removing water. This can be repeated until a product of the desired TBN is obtained.

The overbasing process is well known in the art and typically comprises reacting acidic material with a reaction mixture comprising the
15 organic acid or its metal salt, a metal compound. That acidic material may be a gas such as carbon dioxide or sulfur dioxide, or it may be boric acid. Processes for the preparation of overbased alkali metal sulfonates and phenates are described in EP-A-266034. A process suitable for overbased sodium sulfonates is described in EP-A-235929. A process for making
20 overbased salicylates is described in EP-A-351052.

The overbased metal detergents can be borated. The boron may be introduced by using boric acid as the acidic material used in the overbasing step. However a preferred alternative is to borate the overbased product after formation by reacting a boron compound with the overbased metal
25 salt. Boron compounds include boron oxide, boron oxide hydrate, boron trioxide, boron trifluoride, boron tribromide, boron trichloride, boron acid such as boronic acid, boric acid, tetraboric acid and metaboric acid, boron hydrides, boron amides and various esters of boron acids. Boric acid is preferred. Generally, the overbased metal salt may be reacted with a
30 boron compound at from 50°C to 250°C, in the presence of a solvent such as mineral oil or xylene. The borated overbased alkali metal salt preferably comprises at least 0.5%, preferably from 1% to 5%, by weight boron.

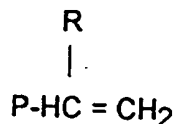
C. THE NITROGEN CONTAINING DISPERSANT

In general the nitrogen containing dispersants comprise an oil solubilizing polymeric hydrocarbon backbone derivatized with nitrogen substituents that are capable of associating with polar particles to be dispersed. Typically, the dispersants comprise a nitrogen containing moiety attached to the polymer backbone often via a bridging group. The nitrogen containing dispersant of the present invention may be selected from any of the well known oil soluble salts, amides, imides, amino-esters, and oxazolines of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

The oil soluble polymeric hydrocarbon backbone is typically an olefin polymer, especially polymers comprising a major molar amount (i.e. greater than 50 mole %) of a C₂ to C₁₈ olefin (e.g., ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene), and typically a C₂ to C₅ olefin. The oil soluble polymeric hydrocarbon backbone may be a homopolymer (e.g. polypropylene or polyisobutylene) or a copolymer of two or more of such olefins (e.g. copolymers of ethylene and an alpha-olefin such as propylene and butylene or copolymers of two different alpha-olefins). Other copolymers include those in which a minor molar amount of the copolymer monomers, e.g., 1 to 10 mole %, is a C₃ to C₂₂ non-conjugated diolefin (e.g., a copolymer of isobutylene and butadiene, or a copolymer of ethylene, propylene and 1,4-hexadiene or 5-ethylidene-2-norbornene).

One preferred class of olefin polymers is polybutenes and specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C₄ refinery stream. Another preferred class of olefin polymers is ethylene alpha-olefin (EAO) copolymers or alpha-olefin homo- and copolymers having in each case a high degree (e.g. >30%) of terminal vinylidene unsaturation. That is, the polymer has the following structure:

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- wherein P is the polymer chain and R is a C₁ - C₁₈ alkyl group, typically methyl or ethyl. Preferably the polymers have at least 50% of the polymer chains with terminal vinylidene unsaturation. EAO copolymers of this type preferably contain 1 to 50 wt.% ethylene, and more preferably 5 to 45 wt.% ethylene. Such polymers may contain more than one alpha-olefin and may contain one or more C₃ to C₂₂ diolefins. Also usable are mixtures of EAO's of low ethylene content with EAO's of high ethylene content. The EAO's may also be mixed or blended with PIB's of various \overline{M}_n 's or components derived from these may be mixed or blended. Atactic propylene oligomer typically having \overline{M}_n of from 700 to 500 may also be used, as described in EP-A-490454.
- Suitable olefin polymers and copolymers may be prepared by cationic polymerization of hydrocarbon feedstreams, usually C₃ - C₅, in the presence of a strong Lewis acid catalyst and a reaction promoter, usually an organoaluminum such as HCl or ethylaluminum dichloride. Tubular or stirred reactors may be used. Such polymerizations and catalysts are described, e.g., in US 4,935,576 and 4,952,739. Fixed bed catalyst systems may also be used as in US 4,982,045 and UK-A 2,001,662. Most commonly, polyisobutylene polymers are derived from Raffinate I refinery feedstreams. Conventional Ziegler-Natta polymerization may also be employed to provide olefin polymers suitable for use to prepare dispersants and other additives.
- Such preferred polymers may be prepared by polymerizing the appropriate monomers in the presence of a catalyst system comprising at least one metallocene (e.g. a cyclopentadienyl-transition metal compound) and preferably an activator, e.g. an alumoxane compound. The metallocenes may be formed with one, two, or more cyclopentadienyl groups, which are substituted or unsubstituted. The metallocene may also contain a further displaceable ligand, preferably displaced by a cocatalyst - a leaving group - that is usually selected from a wide variety of hydrocarbyl groups and halogens. Optionally there is a bridge between the cyclopentadienyl groups and/or leaving group and/or transition metal, which may comprise one or more of a carbon, germanium, silicon,

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phosphorus or nitrogen atom-containing radical. The transition metal may be a Group IV, V or VI transition metal. Such polymerizations and catalysts are described, for example, in US-A-4530914, 4665208, 4808561, 4871705, 4897455, 4937299, 4952716, 5017714, 5055438, 5057475, 5064802, 5096867, 5120867, 5124418, 5153157, 5198401, 5227440, 5241025; EP-A-129368, 277003, 277004, 420436, 520732; and WO-A-91/04257, 92/00333, 93/08199, 93/08221, 94/07928 and 94/13715.

The oil soluble polymeric hydrocarbon backbone will usually have number average molecular weight (\overline{M}_n) within the range of from 300 to 20,000. The \overline{M}_n of the backbone is preferably within the range of 500 to 10,000, more preferably 700 to 5,000 where the use of the backbone is to prepare a component having the primary function of dispersancy. Hetero polymers such as polyepoxides are also usable to prepare components. Both relatively low molecular weight (\overline{M}_n 500 to 1500) and relatively high molecular weight (\overline{M}_n 1500 to 5,000 or greater) polymers are useful to make dispersants. Particularly useful olefin polymers for use in dispersants have \overline{M}_n within the range of from 1500 to 3000. Where the component is also intended to have a viscosity modification effect it is desirable to use higher molecular weight, typically with \overline{M}_n of from 2,000 to 20,000, and if the component is intended to function primarily as a viscosity modifier then the molecular weight may be even higher with an \overline{M}_n of from 20,000 up to 500,000 or greater. The functionalized olefin polymers used to prepare dispersants preferably have approximately one terminal double bond per polymer chain.

The \overline{M}_n for such polymers can be determined by several known techniques. A convenient method for such determination is by gel permeation chromatography (GPC) which additionally provides molecular weight distribution information, see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979.

The oil soluble polymeric hydrocarbon backbone may be functionalized to incorporate a functional group into the backbone of the polymer, or as pendant groups from the polymer backbone. The functional group typically will be polar and contain one or more hetero atoms such as P, O, S, N, halogen, or boron. It can be attached to a saturated

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hydrocarbon part of the oil soluble polymeric hydrocarbon backbone via substitution reactions or to an olefinic portion via addition or cycloaddition reactions. Alternatively, the functional group can be incorporated into the polymer by oxidation or cleavage of a small portion of the end of the polymer (e.g., as in ozonolysis).

Useful functionalization reactions include: halogenation of the polymer at an olefinic bond and subsequent reaction of the halogenated polymer with an ethylenically unsaturated functional compound; reaction of the polymer with an unsaturated functional compound by the "ene" reaction absent halogenation (an example of the former functionalization is maleation where the polymer is reacted with maleic acid or anhydride); reaction of the polymer with at least one phenol group (this permits derivatization in a Mannich Base-type condensation); reaction of the polymer at a point of unsaturation with carbon monoxide using a Koch-type reaction to introduce a carbonyl group in an iso or neo position; reaction of the polymer with the functionalizing compound by free radical addition using a free radical catalyst; reaction with a thiocarboxylic acid derivative; and reaction of the polymer by air oxidation methods, epoxidation, chloroamination, or ozonolysis.

The functionalized oil soluble polymeric hydrocarbon backbone is then further derivatized with a nucleophilic amine, amino-alcohol, or mixture thereof to form oil soluble salts, amides, imides, amino-esters, and oxazolines. Useful amine compounds include mono- and (preferably) polyamines, most preferably polyalkylene polyamines, of about 2 to 60, preferably 2 to 40 (e.g. 3 to 20), total carbon atoms and about 1 to 12, preferably 3 to 12, and most preferably 3 to 9 nitrogen atoms in the molecule. These amines may be hydrocarbyl amines or may be predominantly hydrocarbyl amines in which the hydrocarbyl group includes other groups, e.g., hydroxy groups, alkoxy groups, amide groups, nitriles, imidazoline groups, and the like. Useful amine compounds for derivatizing functionalized polymers comprise at least one amine and can comprise one or more additional amine or other reactive or polar groups. Where the functional group is a carboxylic acid, carboxylic ester or thiol ester, it reacts with the amine to form an amide. Preferred amines are aliphatic saturated amines. Non-limiting examples of suitable amine compounds include: 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-

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diaminohexane; polyethylene amines such as diethylene triamine; triethylene tetramine; tetraethylene pentamine; and polypropyleneamines such as 1,2-propylene diamine; and di-(1,2-propylene)triamine.

Other useful amine compounds include: alicyclic diamines such as
5 1,4-di(aminomethyl) cyclohexane, and heterocyclic nitrogen compounds
such as imidazolines. Mixtures of amine compounds may advantageously
be used such as those prepared by reaction of alkylene dihalide with
ammonia. Useful amines also include polyoxyalkylene polyamines. A
particularly useful class of amines are the polyamido and related amido-
10 amines as disclosed in US 4,857,217; 4,956,107; 4,963,275; and
5,229,022. Also usable is tris(hydroxymethyl)amino methane (THAM) as
described in US 4,102,798; 4,113,639; 4,116,876; and UK 989,409.

Dendrimers, star-like amines, and comb-structure amines may also
be used. Similarly, one may use the condensed amines of Steckel US
15 5,053,152. The functionalized polymer of this invention is reacted with the
amine compound according to conventional techniques as in EP-A 208,560
and US 5,229,022 using any of a broad range of reaction ratios as
described therein.

A preferred group of nitrogen containing dispersants includes those
20 derived from polyisobutylene substituted with succinic anhydride groups
and reacted with polyethylene amines (e.g. tetraethylene pentamine,
pentaethylene, polyoxypropylene diamine), aminoalcohols such as
trimethylolaminomethane, and optionally additional reactants such as
alcohols and reactive metals e.g. pentaerythritol, and combinations
25 thereof).

Also useful as nitrogen containing dispersants are dispersants
wherein a polyamine is attached directly to the long chain aliphatic
hydrocarbon as shown in US 3,275,554 and 3,565,804 where a halogen
group on a halogenated hydrocarbon is displaced with various alkylene
30 polyamines.

Another class of nitrogen-containing dispersants comprises Mannich
base condensation products. Generally, these Mannich condensation
products are prepared by condensing about one mole of an alkyl-
substituted mono- or polyhydroxy benzene with about 1 to 2.5 moles of

carbonyl compounds (e.g., formaldehyde and paraformaldehyde) and about 0.5 to 2 moles polyalkylene polyamine as disclosed, for example, in US 3,442,808. Such Mannich condensation products may include a long chain, high molecular weight hydrocarbon (e.g., \overline{M}_n of 1,500 or greater) on the benzene group or may be reacted with a compound containing such a hydrocarbon, for example, polyalkenyl succinic anhydride as shown in US 3,442,808.

Examples of functionalized and/or derivatized olefin polymers based on polymers synthesised using metallocene catalyst systems are described in publications identified above.

The functionalizations, derivatizations, and post-treatments described in the following patents may also be adapted to functionalize and/or derivatize the preferred polymers described above: US 3,275,554, 3,565,804, 3,442,808, 3,442,808, 3,087,936 and 3,254,025.

The nitrogen containing dispersant can be further post-treated by a variety of conventional post treatments such as boration as generally taught in US 3,087,936 and 3,254,025. This is readily accomplished by treating an acyl nitrogen dispersant with a boron compound selected from the class consisting of boron oxide, boron halides, boron acids and esters of boron acids in an amount to provide from about 0.1 atomic proportion of boron for each mole of the acylated nitrogen composition to about 20 atomic proportions of boron for each atomic proportion of nitrogen of the acylated nitrogen composition. Usefully the dispersants contain from about 0.05 to 2.0 wt. %, e.g. 0.05 to 0.7 wt. % boron based on the total weight of the borated acyl nitrogen compound. The boron, which appears to be in the product as dehydrated boric acid polymers (primarily $(HBO_2)_3$), is believed to attach to the dispersant imides and diimides as amine salts e.g. the metaborate salt of the diimide.

Boration is readily carried out by adding from about 0.05 to 4, e.g. 1 to 3 wt. % (based on the weight of acyl nitrogen compound) of a boron compound, preferably boric acid, which is usually added as a slurry to the acyl nitrogen compound and heating with stirring at from about 135° C. to 190°, e.g. 140°-170° C., for from 1 to 5 hours followed by nitrogen stripping. Or, the boron treatment can be carried out by adding boric acid to a hot

reaction mixture of the dicarboxylic acid material and amine while removing water.

NITROGEN CONTAINING DISPERSANT VISCOSITY MODIFIERS

Viscosity modifiers (or viscosity index improvers) impart high and low
5 temperature operability to a lubricating oil. Viscosity modifiers that function
as dispersants are also known. These multifunctional dispersant viscosity
modifiers may be used to totally or partially replace nitrogen containing
dispersant. In general, these dispersant viscosity modifiers are polymers
as described below that are functionalized (e.g. inter polymers of ethylene-
10 propylene post grafted with an active monomer such as maleic anhydride)
and then derivatized with an alcohol or amine. When the dispersant
viscosity modifier is derivatized with a nitrogen containing group, it is a
source of dispersant nitrogen as contemplated in the present invention.
The lubricant may be formulated with or without a conventional viscosity
15 modifier and with or without a dispersant viscosity modifier. When the
lubricant contains a dispersant viscosity modifier that contains nitrogen,
that nitrogen is included in total dispersant nitrogen added to the
basestock.

Suitable compounds for use as viscosity modifiers are generally high
20 molecular weight hydrocarbon polymers, including polyesters. Oil soluble
viscosity modifying polymers generally have weight average molecular
weights of from about 10,000 to 1,000,000, preferably 20,000 to 500,000,
as determined by gel permeation chromatography or light scattering
methods.

25 Representative examples of suitable viscosity modifiers are
polyisobutylene, copolymers of ethylene and propylene and higher alpha-
olefins, polymethacrylates, polyalkylmethacrylates, methacrylate
copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl
compound, inter polymers of styrene and acrylic esters, and partially
30 hydrogenated copolymers of styrene/ isoprene, styrene/butadiene, and
isoprene/butadiene, as well as the partially hydrogenated homopolymers of
butadiene and isoprene and isoprene/divinylbenzene.

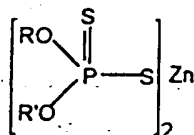
In general, viscosity modifiers that function as dispersant viscosity
modifiers are polymers as described above that are functionalized (e.g.

inter polymers of ethylene-propylene post grafted with an active monomer such as maleic anhydride) and then derivatized with an alcohol or amine. Description of how to make such dispersant viscosity modifiers are found in US 4,089,794, 4,160,739, and 4,137,185. Other dispersant viscosity
 5 modifiers are copolymers of ethylene or propylene reacted or grafted with nitrogen compounds such as shown in US 4,068,056, 4,068,058, 4,146,489, 4,149,984, US 5,427,702 and US 5,424,367

D. METAL DIHYDROCARBYL DITHIOPHOSPHATES

Dihydrocarbyl dithiophosphate metal salts are frequently used as
 10 anti-wear and antioxidant agents. While the metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, manganese, nickel or copper the zinc and molybdenum salts are most commonly used in crankcase lubricants. In the present invention, minimizing the amount of added nitrogen requires a particularly strong antiwear system. Typically the
 15 lubricant will have from 0.1 to 10, preferably 0.2 to 2 wt. %, based upon the total weight of the lubricating oil composition of zinc dihydrocarbyl dithiophosphate. These compounds may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5
 20 and then neutralizing the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are
 25 entirely primary in character. To make the zinc salt any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to use of an excess of the basic zinc compound in the neutralization reaction.

30 In the present invention the preferred zinc dihydrocarbyl dithiophosphates are oil soluble salts of dihydrocarbyl dithiophosphoric acids represented by the following formula:



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wherein R and R' may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R') in the dithiophosphoric acid will generally be about 5 or greater. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates. At least about 50 (mole) % of the alcohols used to introduce hydrocarbyl groups into the dithiophosphoric acids are secondary alcohols. Conveniently at least 10 percent of the hydrocarbyl groups is primary. Keeping the amount of secondary hydrocarbyl groups to between 50 and 70 mole percent gives good wear performance thereby enabling reduction of the amount of dispersant nitrogen and detergent without so adversely impacting performance in fuel economy tests that the lubricant can not meet modern specifications. Most conveniently the hydrocarbyl groups are balanced in this a fashion and the total amount of phosphorus is kept below 0.1 wt % as measured by the X-ray fluorescence spectroscopic method described in ASTM D4927

D. Other Additives

Additional additives are typically incorporated into the compositions of the present invention. Examples of such additives are antioxidants, friction modifiers, rust inhibitors, anti-foaming agents, demulsifiers, pour point depressants, and viscosity modifiers.

Oxidation inhibitors or antioxidants reduce the tendency of mineral oils to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by viscosity growth. Such oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C₅ to C₁₂ alkyl side chains, oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons, phosphorous esters, metal thiocarbamates, oil soluble aromatic amines having at least

two aromatic groups attached directly to one amine nitrogen, and oil soluble copper compounds as described in US 4,867,890, and molybdenum containing compounds.

Friction modifiers may be included to improve fuel economy. Oil-soluble alkoxylated mono- and diamines are well known to improve boundary layer lubrication. The amines may be used as such or in the form of an adduct or reaction product with a boron compound such as a boric oxide, boron halide, metaborate, boric acid or a mono-, di- or trialkyl borate. Other friction modifiers are known. Among these are esters formed by reacting carboxylic acids and anhydrides with alkanols. Other conventional friction modifiers generally consist of a polar terminal group (e.g. carboxyl or hydroxyl) covalently bonded to an oleophilic hydrocarbon chain. Esters of carboxylic acids and anhydrides with alkanols are described in US 4,702,850. Examples of other conventional friction modifiers are described by M. Belzer in the "Journal of Tribology" (1992), Vol. 114, pp. 675-682 and M. Belzer and S. Jahanmir in "Lubrication Science" (1988), Vol. 1, pp. 3-26.

Rust inhibitors selected from the group consisting of nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids may be used.

Copper and lead bearing corrosion inhibitors may be used, but are typically not required with the formulation of the present invention. Typically such compounds are the thiadiazole polysulfides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Derivatives of 1,3,4 thiadiazoles such as those described in U.S. Pat. Nos. 2,719,125; 2,719,126; and 3,087,932; are typical. Other similar materials are described in U.S. Pat. Nos. 3,821,236; 3,904,537; 4,097,387; 4,107,059; 4,136,043; 4,188,299; and 4,193,882. Other additives are the thio and polythio sulfenamides of thiadiazoles such as those described in UK Patent Specification No. 1,560,830. Benzotriazoles derivatives also fall within this class of additives. When these compounds are included in the lubricating composition, they are preferably present in an amount not exceeding 0.2 wt % active ingredient.

A small amount of a demulsifying component may be used. A preferred demulsifying component is described in EP 330,522. It is obtained by reacting an alkylene oxide with an adduct obtained by reacting

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a bis-epoxide with a polyhydric alcohol. The demulsifier should be used at a level not exceeding 0.1 mass % active ingredient. A treat rate of 0.001 to 0.05 mass % active ingredient is convenient.

5 Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives which improve the low temperature fluidity of the fluid are C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers and polyalkylmethacrylates.

10 Foam control can be provided by many compounds including an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

The viscosity modifier functions to impart high and low temperature operability to a lubricating oil. The viscosity modifier used may have that sole function, or may be multifunctional. As discussed above
15 multifunctional viscosity modifiers that also function as dispersants are also known and may be prepared as described above for dispersants.

Suitable compounds for use as monofunctional viscosity modifiers are generally high molecular weight hydrocarbon polymers, including polyesters. Oil soluble viscosity modifying polymers generally have weight
20 average molecular weights of from about 10,000 to 1,000,000, preferably 20,000 to 500,000, which may be determined by gel permeation chromatography (as described above) or by light scattering.

Representative examples of suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate
25 copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter polymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/ isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of
30 butadiene and isoprene and isoprene/divinylbenzene.

The viscosity modifier used in the invention will be used in an amount to give the required viscosity characteristics. Since they are typically used in the form of oil solutions the amount of additive employed

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will depend on the concentration of polymer in the oil solution comprising the additive. However by way of illustration, typical oil solutions of polymer used as viscosity modifiers are used in amount of from 1 to 30% of the blended oil. The amount of VM as active ingredient of the oil is generally
 5 from 0.01 to 6 wt%, and more preferably from 0.1 to 2 wt%.

Some of the above-mentioned additives can provide a multiplicity of effects; thus for example, a single additive may act as a dispersant-oxidation inhibitor. This approach is well known and does not require further elaboration.

10 When lubricating compositions contain one or more of the above-mentioned additives, each additive is typically blended into the base oil in an amount which enables the additive to provide its desired function. Representative effective amounts of such additives, when used in crankcase lubricants, are listed below. All the values listed are stated as
 15 mass percent active ingredient.

ADDITIVE	MASS % (Broad)	MASS % (Preferred)
Dispersant	0.1 - 20	1 - 8
Overbased metal detergents	0.1 - 15	0.2 - 1.5
Neutral metal detergents	0 - 5	0 - 0.5
Corrosion Inhibitor	0 - 5	0 - 1.5
Metal dihydrocarbyl dithiophosphate	0.1 - 6	0.1 - 1
Supplemental anti-oxidant	0 - 5	0.01 - 1.5
Pour Point Depressant	0.01 - 5	0.01 - 1.5
Anti-Foaming Agent	0 - 5	0.001 - 0.15
Supplemental Anti-wear Agents	0 - 0.5	0 - 0.2
Friction Modifier	0 - 5	0 - 1.5
Viscosity Modifier	0.01 - 6	0 - 4
Mineral or Synthetic Base Oil	Balance	Balance

The components may be incorporated into a base oil in any convenient way. Thus, each of the components can be added directly to the oil by dispersing or dissolving it in the oil at the desired level of concentration. Such blending may occur at ambient temperature or at an
 20 elevated temperature. Alternatively subcombinations of additives can be

prepared and blended together. For purposes of the present invention, the blend order of components does not matter.

Preferably all the additives except for the viscosity modifier and the pour point depressant are blended into a concentrate or additive package which is commonly known a "detergent inhibitor package", that is subsequently blended into basestock to make finished lubricant. Use of such concentrates is conventional. The concentrate will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration in the final formulation when the concentrate is combined with a predetermined amount of base lubricant.

Preferably the concentrate is made in accordance with the method described in US 4,938,880. That patent describes making a premix of dispersant and metal detergents that is pre-blended at a temperature of at least about 100°C. Thereafter the pre-mix is cooled to at least 85°C and the additional components are added.

The final formulations may employ from 2 to 5 mass % and preferably 3 to 5 mass %, typically about 3.5 to 4 mass % active ingredient additives in a concentrate or additive package with the remainder being base oil.

When determining whether the one or more detergents that collectively comprise the detergent system meets the definition of the present invention, base contribution of the inorganic and organic salts present in each of the detergents added must be determined. The compositions of metal detergents are not known with certainty. For example sulfurized metal phenates are generally described as bis-thio-phenates with sulfur linkages of varying lengths. In fact the number of phenolic groups actually linked together is not known with certainty. Similarly, the amount of phenol assumed to convert to a metal salt is often assumed to be 100%. In fact the degree of the neutralization depends on the acidity of the phenol and the acidity of the neutralizing base. Further the equilibria established when the component is made shift whenever the component is blended with other materials containing strong bases. For these reasons, the amounts of carbonate, sulfonate, and phenolic hydroxide present in a lubricant and their contribution to the TBN of the finished lubricant, are inferred from the amounts present in the individual

components that are blended together by determining how much of each moiety is present in the individual components, adjusting for the dilution that occurs when the components are blended into the finished lubricant, and adding together the amounts of the various moieties. In the same way
5 the TBN contribution from each component can be measured as described below, the contribution can be adjusted for dilution in the finished lubricant, and the sum of the contributions will correspond to that of the finished lubricant.

10 The amounts of the individual moieties are in turn inferred from the charge ratios of raw materials used to make the detergents or by resort to analytical methods that can determine detectable moieties allowing inference of the remaining moieties.

ASTM D2896 describes the industry standard method for determining total base number of a fluid. The method titrates the fluid to
15 determine the equivalent amount of KOH required to neutralize a strong acid. The units of TBN determined by ASTM 2896 are mg KOH/gm sample. This method is used to determine the TBN of the finished lubricant. It may also be used to determine the total TBN of phenates, sulfurized phenates, and salicylates. When the method is used on a metal
20 sulfonate, the base concentration of the organic soap is not measured, so the ASTM D2896 TBN for a sulfonate detergent reflects only the TBN contributed by overbasing. Determination of the TBN contribution from the sulfonate salt may be possible with the liquid chromatography method described in ASTM 3712

25 For salts of organic acids other than sulfonates allocating the total TBN of the component between overbasing and organic salts requires that the number of moles of salt present must be derived. Thus for phenates and carboxylates (including salicylates) the total amount of metal must be determined and allocated between organic and inorganic acids using a
30 metal ratio. The total amount of metal present is conveniently determined by inductively coupled plasma atomic emission spectrometry – ASTM D4951. Metal ratio is defined as the total amount of metal present divided by the amount of metal in excess of that required to neutralize any organic acid present, i.e. the amount of metal neutralizing inorganic acids. Metal
35 ratios are quoted by manufacturers of commercial detergents and can be

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determined by a manufacturer having knowledge of the total amount of salts present and the average molecular weight of the organic acid. The amount of metal salt present in a detergent may be determined by dialyzing the detergent and quantifying the amount of the residue. If the average

5 molecular weight of the organic salts is not known, the residue from the dialyzed detergent can be treated with strong acid to convert the salt to its acid form and analyzed by a combination of chromatographic methods, proton NMR, and mass spectroscopy and correlated to detergents having known properties. More particularly, the detergent is dialyzed and then the

10 residue is treated with strong acid to convert any salts to their respective acid form. At that point the hydroxide number of the mixture can be determined by the method described in ASTM D1957. If the detergent contains non-phenolic hydroxyl groups on the phenolic compound (e.g., alcoholic derivatives of ethylene glycol used in manufacture of commercial

15 phenates or carboxylic acid groups on salicylic acid), separate analyses must be conducted to quantify the amounts of those hydroxyl groups so that the hydroxide number determined by ASTM D1957 can be corrected. Suitable techniques to determine the quantity of non-phenolic hydroxyl groups include analyses by mass spectroscopy, liquid chromatography,

20 and proton NMR and correlation to compounds having known properties.

A second method for deriving the number of moles of metal salt of an organic acid present assumes that all of the organic acid charged to make the component is in fact converted to the salt. In practice these two methods can give slightly different results, but both are believed to be

25 sufficiently precise to allow determination of the amount of salt present to the precision required to practice the present invention.

Once the ASTM D2896 TBN of the component and the TBN contribution of the phenate and salicylate is determined, the TBN contribution of the overbasing is determined by subtracting. For sulfonates,

30 the ASTM D2896 TBN is the TBN contribution for the inorganic salt and can be used directly to determine the ratio of the TBN contributed by the inorganic salts to the TBN contributed by the organic salt.

Determining the amount of dispersant nitrogen is readily accomplished by analyzing the dispersant components for nitrogen and

35 adjusting for their respective treat rates in the final lubricant. Alternatively,

a finished lubricant can be dialyzed to separate polymeric components (comprised primarily of viscosity modifier, dispersant, and pour point depressant) from basestock and lower molecular weight additives. The nitrogen content of the dialysis residue is determined a by the method
5 described in ASTM D5291.

The hydrocarbyl content of zinc dihydrocarbyl dithiophosphates (ZDDP) may be determined from molar charge ratios of alcohols to make the dihydrocarbyl dithiophosphoric acid or by analyzing a finished component or a finished oil. To separate ZDDPs from a finished lubricant
10 or detergent inhibitor package, a sample is solvent extracted, for example with methanol. The extract is digested with acid (e.g. phosphoric acid). The acid is neutralized with potassium hydroxide and a further extraction with a suitable solvent (e.g. hexane) is performed. The residual alcohols can then be analyzed by gas chromatography. The amounts of various
15 alcohols present can be determined by comparing the chromatographic to those of known alcohols.

The invention will now be described by way of illustration only with reference to the following examples. In the examples, unless otherwise noted, all treat rates of all additives are reported as mass percent active
20 ingredient.

Examples 1 and 2

Formulated lubricants containing polyisobutenyl succinimide dispersant, zinc dihydrocarbyldithiophosphate, antioxidants, antifoamant, demulsifier, olefin copolymer viscosity modifier in an amount to make the
25 oils SAE 5W-30 oils and detergents as described in Table are tested for their ability to neutralize strong acid. In the test a 20 gram sample of the oil is placed into a 50 ml reaction flask. The flask immersed in a 60°C constant temperature bath. The flask is fitted with a pressure transducer that measures the pressure of the volume above the surface of liquid every
30 10 seconds. After the temperature of the oil has reached the temperature of the bath, 5 molar sulfuric acid is added in amount greater than the total amount required to neutralize all of the detergent added to the oil (which may be calculated readily from the TBN's of the detergents adjusted for treat rate or from the TBN of the sample). Then the pressure of the volume
35 above the liquid is measured. As the sulfuric acid is neutralized by the

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colloid, carbon dioxide evolves thereby increasing the pressure in the volume above the surface of the liquid. Since this pressure increase is directly related to the amount of CO₂ generated, pressure increase is a good measure of the ability of the oil neutralize strong acids. An oil is considered to have good acid neutralization properties if it can increase the pressure in the volume above the oil in a 50 ml flask by 2 psi in about 65 seconds or less.

In Example 1 the overbased detergent is a 400 TBN magnesium sulfonate having predominately carbonate overbasing and a metal ratio of 14.3. The additional detergents used in some oils are a 135 TBN calcium phenate with hydroxide overbasing and a 64 TBN calcium salicylate with no overbasing. All treat rates are expressed as weight percent active ingredient. Table 1 demonstrates that the availability of the overbasing in the colloid is decreased when too much organic salt is present. The results are shown in Table I.

Table I

Example	1A	1B	1C	1D	1E	1F	1G	1H	1I
Mg Sulfonate, 400 TBN	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Ca Salicylate, 64 TBN	1	0	0.5	0	0	0	0	0	0
Sulfurized Ca Phenate, 135 TBN	0	2	0	1.02	0.612	0.51	0.255	0.102	0
TBN from inorganic salts/ moles organic salts	807	1213	1457	1537	2095	2336	3425	5000	7479
Time to reach 2 PSI, seconds	84	78	78	77	58	79	67	52	52

In Example 2 the overbased detergent is a 345 TBN calcium salicylate with predominately carbonate overbasing. The additional detergent is a 64 TBN calcium salicylate having no overbasing. Table 2 demonstrates that decreasing the amount of organic salt present increases the rate at which the colloid can neutralize acid. All treat rates are expressed as weight percent active ingredient.

Table II

Example	2A	2B	2C
Magnesium Salicylate, 345 TBN	0.6	0.6	0.6
Calcium Salicylate, 64 TBN	1	0.5	0
TBN from inorganic salts/ moles organic salts	778	1213	2757
Time to reach 2 PSI, seconds	80	74	66

Example 3

The unexpected impact of dispersant nitrogen on the ability of the colloid to neutralize acid is demonstrated using the procedure described in Examples 1 and 2 except that the time to reach 1 psi pressure increase is

used as the end point. The detergent is a 400 TBN magnesium sulfonate with predominately carbonate overbasing. Dispersant A is a polyisobutenyl succinimide made by reacting a polyisobutenyl succinic anhydride with polyamine where the PIBSA to polyamine molar ratio is 2.1 to 1.

- 5 Dispersant B is a polyisobutenyl succinimide made by reacting a polyisobutenyl succinic anhydride with polyamine where the weight ratio of PIBSA to polyamine is 1.5. All treat rates are expressed as weight percent active ingredient. Table 3 shows the adverse impact of increasing dispersant nitrogen on acid neutralization rates.

Table III

	3A	3B	3C	3D
Magnesium Sulfonate, 400 TBN	0.57	0.57	0.57	0.57
Polyisobutenyl succinimide A	2.02	0	3.03	0
Polyisobutenyl succinimide B	0	2.02	0	3.03
Total Dispersant Nitrogen, gm percent	0.0616	0.0852	0.0924	0.1278
Time to reach 1 PSI, seconds	26	30	31	35

Claims:

1. A crankcase lubricant comprising an oil of lubricating viscosity having added thereto
 - 5 a detergent system comprising one or more alkali or alkaline earth metal salts of an oil soluble organic acid selected from the group consisting of sulfonic acids, phenols, sulfurized phenols, and carboxylic acids wherein at least one metal salt is overbased and the ratio of TBN from inorganic salts to moles of organic salts is at least 2500,
 - 10 between about 0.0073 and 0.053 grams per 100 grams finished lubricant dispersant nitrogen, and
 - one or more zinc dihydrocarbyldithiophosphate wherein at least half of the hydrocarbyl groups are secondary alkyl groups
 - wherein the ASTM D2896 TBN of the lubricant is not greater than about 5.
- 15 2. The lubricant of Claim 1 wherein the detergent system comprises an overbased salt of an oil soluble magnesium sulfonate and the ratio of TBN from inorganic salts to moles of organic salts is at least 4,200.
3. The lubricant of Claim 1 wherein the detergent system comprises an overbased salt of an oil soluble magnesium sulfonate and the
 - 20 ratio of TBN from inorganic salts to moles of organic salts is at least 7,000.
4. The lubricant of Claim 1 wherein the dispersant nitrogen is added as an dispersant made by reacting a substituted succinic acylating agent with an amine wherein the substituent on the succinic acylating agent has a \overline{M}_n of at least 1300.
- 25 5. The lubricant of Claim 1 wherein the dispersant nitrogen is added at least in part as a nitrogen containing multifunctional viscosity modifier.
6. The lubricant of Claims 1 or 3 wherein at least 10 mole % of the hydrocarbyl groups on the zinc dialkydithiophosphate are primary.
- 30 7. The lubricant of Claim 1 wherein the detergent system comprises an overbased salt of an oil soluble magnesium salicylate and the ratio of TBN from inorganic salts to moles of organic salts is at least 3000.

8. The lubricant of Claim 6 wherein the total phosphorus level is less than 0.1 ppm.

INTERNATIONAL SEARCH REPORT

International Application No
PC/US 96/13637

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C10M163/00 //(C10M163/00,133:52,133:56,137:10,159:20,159:22, 159:24),C10N30:00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C10M		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 686 689 (NIPPON OIL CO.) 13 December 1995 see the whole document ---	1-4
A	EP,A,0 113 045 (HONDA MOTOR CO.) 11 July 1984 see page 14; table 1 ---	1-8
A	EP,A,0 317 354 (EXXON CHEMICAL PATENTS) 24 May 1989 see page 19; table 1 ---	1-8
A	EP,A,0 638 632 (ETHYL PETROLEUM ADDITIVES) 15 February 1995 ---	
A	WO,A,94 12595 (EXXON CHEMICAL PATENTS INC.) 9 June 1994 -----	
<div style="display: flex; justify-content: space-between;"> <input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents:</p> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*A* document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-size: 1.2em;">6 November 1996</div>		Date of mailing of the international search report <div style="text-align: center; font-size: 1.2em;">06.12.96</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016		Authorized officer <div style="text-align: center; font-size: 1.2em;">Hilgenga, K</div>

INTERNATIONAL SEARCH REPORT

Information on patent family members

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